

ELECTRICAL PROPERTIES OF LEAD-OXIDE BASE CHALCOGENIDE (Se) GLASSES

By
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DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST, 1976

ELECTRICAL PROPERTIES OF LEAD-OXIDE BASE CHALCOGENIDE (Se) GLASSES

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
BHARAT KUMAR PANDEY

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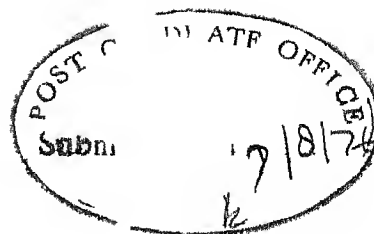
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TO MY
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WHOM I LOVE MOST



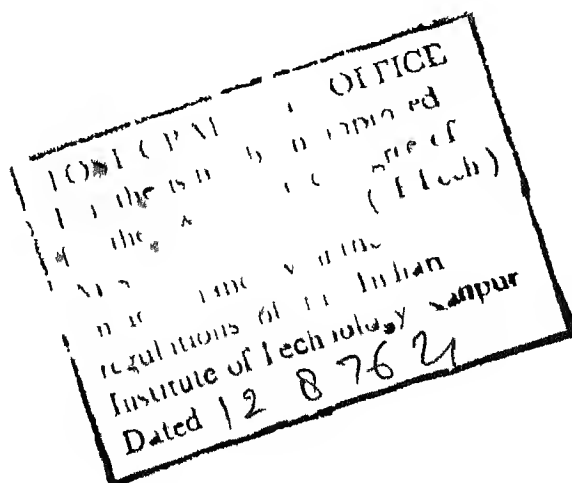
CERTIFICATE

Certified that the work contained in the thesis entitled "'Electrical Properties of Lead oxide base chalcogenide (Se) glasses'" has been carried out by Mr Bharat Kumar Pandey under my supervision and the same has not been submitted elsewhere for a degree

DC

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I wish to express my sincere thanks and gratitude to Dr D Chakravorty for his inspiring and excellent guidance throughout the work

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BHARAT KUMAR PANDEY

SYNOPSIS

An investigation of electrical properties of various glasses of the system $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2$ containing Se alone or Se with either of Bi_2O_3 , Sb_2O_3 and As_2O_3 has been carried out. Bulk resistivity of the glasses were measured as a function of temperature. Silver electrode make non-ohmic contact with these glasses i.e. I-V characteristic of these glasses with Ag electrode is non-linear, while gold electrode make ohmic contacts.

Some glasses show high value of resistivity and variation of resistivity as a function of temperature can be given by the equation $\rho = \rho_0 \exp\left(\frac{A}{kT}\right)$. As the concentration of various components is changed the electrical resistivity drops from $10^9\text{-}10^{12}$ ohm-cm to $10^2\text{-}10^5$ ohm-cm. The variation of resistivity is also very small with temperature. In some glasses the resistivity increases with

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CHAPTER I

INTRODUCTION

The modern development of Technology has created the prerequisites for an extreme expansion of the field of investigation of Physical and Chemical properties of semiconducting materials. Intensive investigations are under way in search of new materials and additional applications are continually being uncovered. The tremendous technological expansion of the past two decades has been based in large part on the continuing interplay between new advances in our fundamental understanding of the electrical properties of these materials and the discovery of new electronic applications of materials in increasingly more complex devices and systems. Some examples will illustrate the great diversity and importance of their applications. Viz¹ switching and memory devices, continuous dynode electron multiplier (channeltran), optical mass memories, phase contrast holograms, high energy particle detectors, infrared lenses, ultrasonic delay lines, microfiche transparencies and transducers.

The draw-backs of crystalline semiconducting materials are the requirement of extreme chemical purity

and chemical attack. Amorphous semiconductors are relatively insensitive to impurities and chemical attack. They can be manufactured with unique chemical, thermal, electrical, magnetic, optical, mechanical and mass transport properties. Due to the favorable physical, chemical, electrical properties and ease with which they can be produced in any form, they have become a popular subject for research and invention.

1.1 Amorphous Semiconductors

Amorphous semiconductors can be classified in three main categories²

1. The first category contains the usual crystalline semiconductors: silicon, germanium, and indium antimonide, etc., which are obtained in the amorphous state as thin films from the vapour phase.

2. The second category contains chalcogenide glasses; these are made up of group VI elements (sulphur, selenium, tellurium) alone or in combination with the group V elements (phosphorus, arsenic, antimony and bismuth).

3. Oxide glasses containing transition metal elements fall in the third group of amorphous semiconductors^{3,4,5}. Alkali borosilicate glasses containing selenium, bismuth oxide, and antimony oxide

come under this category^{6 7}

Amorphous semiconductors behave similar to intrinsic semiconductors. Their low value of conductivity enables one to observe high field effects without excessive heating.

The general electrical behaviour of oxide glasses should be reviewed as the present investigation deals with lead oxide glass system.

1.2 Oxide Glasses

Various oxide glasses show semiconducting behaviour. Soda-silica and alkali borosilicate glasses show ionic conductivity where Na^+ ions are the charge carriers. Stevels⁽⁸⁾ derived the following equation for the ionic conduction in glasses

$$j = \frac{6 kT}{\gamma b a^2 e^2 n} (\exp E/kT) \quad (1)$$

Where γ is the vibrational frequency, b is the number of adjacent wells an ion can jump into, a is the average jump distance, n is the number of mobile ions per cc and E is the energy barrier. From the above equation it is obvious that $\log j$ vs $\frac{1}{T}$ plot will be a straight

The addition of an oxide of a higher valent metal like calcium, lead to an alkali silicate glass

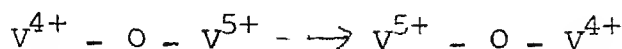
leads to a decrease in ionic mobility of the alkali ion⁽⁹⁾ When a second alkali oxide is added to an alkali silicate glass the conductivity decreases sharply⁽¹⁰⁾ Measurements of diffusion coefficients in such glasses show that the mobility of each ion is decreases by the addition of others⁽¹¹⁾ The decrease in conductivity results from these reductions in mobility, but the reasons for the mobility reduction are not clear

Other category of oxide glasses includes glass systems having oxides of transition metal as one of the constituents These glasses show electronic conductivity

Bulk electronic conduction in $P_2O_5-V_2O_5$ glasses was reported by enton, Rawson and Stanvorth⁽¹²⁾ in 1954 Various other oxide glasses like vanadate - phosphate Vanadate- ~~germanate~~ were studied by Mackenzie^(13 14) Han-blen et al⁽¹⁵⁾ ~~Munakata~~^(16, 17) Bayutan et al⁽¹⁸⁾ and Ioffe and Regel⁽¹⁹⁾ Some Germanate-Vanadate-Phosphate glasses have been studied by Janakirama Rao⁽²⁰⁾ Iron-oxide based glasses have been studied by Hansen⁽²¹⁾ and Mackenzie⁽²²⁾ The conduction in most of these glasses with shown to be the transfer of an electron (and/or Hole) between ions

of same transition metal in different valance states

e g



Murthy⁽⁷⁾ and Bandyopadhyay⁽²³⁾ showed independently that introduction of B_2O_3 in $Na_2O-B_2O_3-SiO_2$ system indecrease electronic conduction and memory switching Devendra⁽²⁴⁾ reported the similar behaviour when he

introduce d Sb_2O_3 in $Na_2O-B_2O_3-SiO_2$ oxide glass system

Kharyuzov and Efimov⁽²⁵⁾ reported that in As-Ge-Si glass system introduction of Pb nearly lead to displacement of the extremal points on the $\log \rho$ vs $\frac{1}{T}$ curve without changing their forms

But in Iron oxide containing silicate glass the conductivity decrease tenfold when the PbO content is doubled as reported by Kuznetsov & Tsekhomskii⁽²⁶⁾ also Jones⁽²⁷⁾ said that substituting PbO increases conductivity and gave reasons

1 3 Selenium

Atomic no 34 Atomic wt 78.76 valance state $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$ appears in 6 allotropic form Melting point $217^\circ C$ and boiling point $685^\circ C$ and

and electrical resistivity 10^{10} to 10^{13} depending upon the form (28-29) But for Trigonal single crystal at room temperature = 10^{+6} to 10^{+5} ohm cm^{-1} Conductivity can not be enhanced by impurity but can increase by lattice defect The V-I's ohmic at low At low temperature curve is strongly voltage dependent

1 4 Mode of Conduction in Amorphous Semiconductors

In amorphous and liquid semiconductors transport in delocalised electronic states for which the mean free path is of the same order as the interatomic spacing and transport by thermally activated hopping between localised states are the modes of conduction that occur This is similar to the hopping or band like conduction with short ^{mean} free path in a heavily doped crystalline semiconductors

In the chalcogenide glasses electronic conduction has been described as occurring in an energy band as in crystalline broad band semiconductors Theories of this type of conduction have been developed by Mott (30-32) and Coworkers Due to disordered state of the material there are continuous densities of states, and therefore the validity of following equation is difficult to understand

$$\sigma = \sigma_0 \exp \left(- \frac{\phi}{kT} \right) \quad (2)$$

The conductivity of amorphous semiconductor varies with temperature according to above equation

1.5 Anderson Transition

Anderson⁽³³⁾ showed that in noncrystalline solid, if certain condition of random potential for the electron is satisfied, then the electronic energy states will be localised and therefore the conduction is due to hopping of electrons between these localised states

If the critical Anderson condition is not satisfied states will still be localized in the tail of the band⁽³⁴⁾. The energy which separates the extended states with the localized states in bands are called mobility edges (E_C and E_V). If Fermi-level E_F lies below E_C , that is in the region of localized states, the conduction will be either due to the thermally activated hopping between the localized states or due to excitation of electrons from E_F to E_C . Conduction may also occur by both the processes and the conductivity follows the same equation where ϕ may have different values. If $E_C - E_F$ changes its sign due to change in structure or the composition of the glass E_F reaches in the region

of extended states and the electron behaves as an itinerant electron and conductivity will show the same behaviour as in case of metals. This phenomenon is known as Anderson transition. The material shows a change from semiconducting behaviour to metallic behaviour.

Electrical Conduction in Lead Glasses

Kharyuzov and Efil'mov⁽²⁵⁾ worked on As-Ge-Pb-Se systems. They varied the Pb content upto 5 atomic % and reported that the introduction of lead merely leads to displacement of the extremal points on the curves without changing their form. Kudashev⁽⁴¹⁾ suggested in lead borate glasses, that three different positions can be occupied by the lead ion in borate glasses. The lead ions may be between two oxygen atoms with unsaturated valences. Such ions strengthen the glass structure. They can not be involved in transport of current. In second case the lead ions may be attached to a single oxygen atom with unsaturated valence. This ion is bound less strongly to the glass structure than in case I but the bond is still fairly strong and the energy required to break it is relatively high. Therefore at low temperature this type of ions have no appreciable influence. In third case the lead ions are not bound to any particular atoms and can easily move within the unit cell of the structure.

net work or pass into neighboring cells. Direct jump of such ions into neighboring cells results in conduction of current.

In lead, silicate glasses containing Fe_2O_3 the effect of variation of PbO content on the resistance value of the glasses were studied and reported by Kuznetsov and Tsekhomskii⁽²⁶⁾. They concluded that since the radius of lead ion (1.32 Å) is less than that of the barium ion (1.43 Å), lead glasses have higher conductivity than barium glasses. The decrease of conductivity with increasing content of modifying oxide in the glass can be explained similarly. They also reported that with the same iron oxide content (10 mole %) the conductivity decreased tenfold when the PbO content is doubled.

Grechanik⁽³⁵⁾ assumed conduction in alkali-free lead glasses to be due to Pb^{2+} ions. It has been shown by Milnes and Isard⁽³⁶⁾ that electric conduction in alkali-free lead silicate glasses is affected by the residual 'water' content of the glass. Increase in OH^- ion concentration showed increase in conductivity and decrease in activation energy. Hughes and Isard⁽⁴²⁾ suggested that the conduction mechanism in the alkali-free lead oxide glasses is either electronic or by means of H^+ ion impurity.

In the present study first we selected the $B_2O_3-SiO_2$ glass system and tried to put Se metal in it. But it was very difficult to achieve sufficiently big size samples for measurement. Then we tried $B_{12}O_3-B_2O_3$ glass system, but again we fail to get stable glasses. These glasses were highly phase separated glasses and layers were coming out easily.

At last we selected the lead oxide glass system. Lead silicate glasses were reported to have very high resistivity and it was worth ^{to} trying to put different metal oxides and metal particle in this glass matrix and observe the effect. For putting the Se metal in we were interested in getting low melting temperature glasses because Se has got the low melting point and gets easily oxidise. $PbO-ZnO-B_2O_3-SiO_2$ systems were reported to have lower melting point ($650^{\circ}C$). Hence we selected above mentioned glass system and put the metal Se $B_{12}O_3$, Sb_2O_3 and As_2O_3 and tried to observe the change in resistivity value. Because all of these oxides ($B_{12}O_3$, Sb_2O_3 and As_2O_3) and Se metal were shown the lowering effect in $B_2O_3-SiO_2$ glass, hence we expected that similar behaviour will be shown with the $PbO-ZnO-B_2O_3-SiO_2$ system.

CHAPTER II

STATEMENT OF THE PROBLEM

The glasses of the system $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2$ were found to show very high resistivity but have the advantage of lower melting temperature and ease of formation. Glasses containing Bi_2O_3 , Sb_2O_3 and As_2O_3 were found to have interesting electrical properties like low resistivity values and switching.

The purpose of present investigation was to study the characteristics of this hetero-phase glass system as a function of composition of the constituents. Compositions of the glasses chosen for study are given in Table I. Following measurements have been made on these glasses:

- 1 Variation of resistivity of glasses $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Se}$ with the varying content of Se and temperature
- 2 Variation of resistivity of glasses $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Bi}_2\text{O}_3\text{-Se}$ with temperature and varying composition of Bi_2O_3 and Se
- 3 Variation of resistivity of glasses $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Sb}_2\text{O}_3\text{-Se}$ with temperature and varying composition of Sb_2O_3 and Se

- 4 Variation of resistivity of glasses $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-As}_2\text{O}_3\text{-Se}$ with temperature and varying composition of As_2O_3 and Se
- 5 Variation of resistivity of glasses $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Se}$ with temperature and varying composition of ZnO and B_2O_3
- 6 Variation of resistivity of glasses $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Se-Bi}_2\text{O}_3$ with temperature and varying composition of PbO and SiO_2
- 7 Variation of resistivity of glasses $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Se-Sb}_2\text{O}_3$ with temperature and varying composition of PbO and SiO_2
- 8 Variation of resistivity of glass $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Se-As}_2\text{O}_3$ with temperature and varying composition of PbO and SiO_2

CHAPTER III

EXPERIMENTAL

3 1 Preparation of Glass

The composition (mole %) of the glasses which were prepared for investigation are given in Table I. All the glasses are having PbO, ZnO, SiO₂ and B₂O₃ as base constituents and selenium or Se with either of Bi₂O₃, Sb₂O₃, As₂O₃ as additional constituents. Calculated amount of reagent grade materials were weighed and mixed thoroughly. The mixture was then transferred to alumina crucible and heated in SiC globar electrically heating furnace to temperature upto 700° to 900°C. At this temperature the melt was kept for half an hour and air quenched to 300°C inside the annealing furnace in the Al molds. Since density of PbO is quite high, PbO remains near the bottom of the crucible. To homogenize the melt, it was stirred before casting. Annealing of the glass, was done for about half an hour at 300°C and then it was furnace cooled to room temperature. The glasses were quenched in the furnace to 300°C because if it is quenched to room temperature the strain and cracks develop rapidly and glass breaks into small pieces before transferring to annealing furnace.

TABLE No 1

Composition of Glasses

Glass No.	Pbo	Zno	B ₂ O ₃	SiO ₂	B ₂ O ₃	Sb ₂ O ₃	As ₂ O ₃	Se	c	Gr-oup
1	51.9	19 2	22.4	6.5	-	-	-	-	-	
2	51 9	14 2	22 4	6 5	-	-	-	5	-	I
3	51 9	14 2	22 4	6	-	-	-	5	0.5	
4	58	14	12	6	-	-	-	10	-	
5	57	10	22	6	-	-	-	5	-	II
6	60	14	15	6	-	-	-	5	-	
7	60	14	17	6	-	-	-	3	-	III
8	60	14	19	6	-	-	-	1	-	
9	54	10	22	6	5	-	-	3	-	
10	54	10	22	6	3	-	-	5	-	
11	54	10	22	6	-	5	-	3	-	IV
12	54	10	22	6	-	3	-	5	-	
13	54	10	22	6	-	-	5	3	-	
14	54	10	22	6	-	-	3	5	-	
15	50	10	22	10	5	-	-	3	-	
16	45	10	22	15	5	-	-	3	-	V
17	50	10	22	10	-	5	-	3	-	
18	45	10	22	15	-	5	-	3	-	

3 2 Specimen Preparation

The glasses were cut into small pieces. The glass pieces were ground and polished to a thickness of 0.2 to 0.9 mm with SiC powder of mesh numbers 120, 240, 400, 600 and 800. After polishing the specimens were washed with acetone.

Gold electrodes were deposited on both sides of the specimens by vacuum evaporation technique. On some glasses Ag electrodes were also made with silver paints. But the specimen thus prepared using Ag electrodes were showing non ohmic behaviour. The area of gold electrodes are in the range of 0.5 cm^2 to 3.5 cm^2 . Copper wire were cemented to the gold electrodes with the help of silver cement. To give mechanical support and strength to the specimens, they were sandwiched between the glass slides with the help of araldite.

3 3 Resistivity Measurements

High resistive samples were measured with the help of General radio electrometer or ECIL picoammeter. Schematic circuit diagram is given in Fig 1. For low resistive samples resistance were measured by connecting standard resistance in series with samples. The drop across the standard resistance and voltage applied

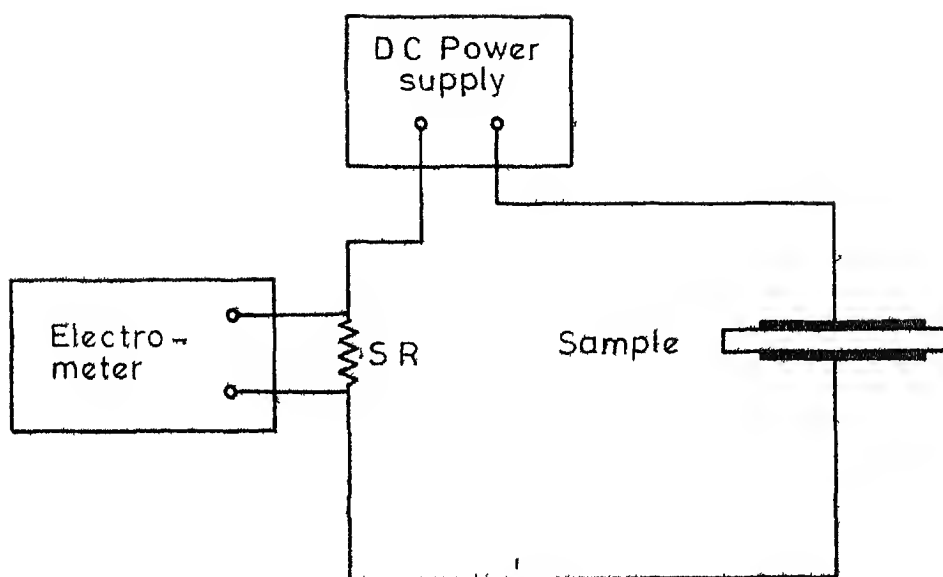


Fig 1 Schematic circuit diagram for resistivity measurement

were measured to get the value of resistance of the samples. To achieve the better accuracy the value of standard resistance was kept to same order of magnitude as that of sample.

For high temperature measurements of resistance samples were kept in a horizontal electrically heating wire wound tube furnace. Inside the refractory tube there was kept a stainless steel tube to provide proper electrical shielding. As Se glasses were reported to have photoelectric effect, care was taken to close the tube mouth from both the ends to avoid such effect. Temperature was raised in steps with the help of APIAB temperature controller and measurements were taken after the stabilization of temperature. The highest temperature selected for measurement was 200°C to minimise high temperature annealing and crystallization of glass samples as the glasses were low temperature melting glasses. Temperature was measured using a potentiometer and chrome-alumel thermocouple.

Low temperature measurements were carried out in a low temperature cell. A schematic representation of this cell is shown in Fig. 2. Liquid nitrogen was used in Dewar flask. Temperature was controlled by the steady state flow of nitrogen vapors produced by an electrically heated filament dipped in liquid nitrogen.

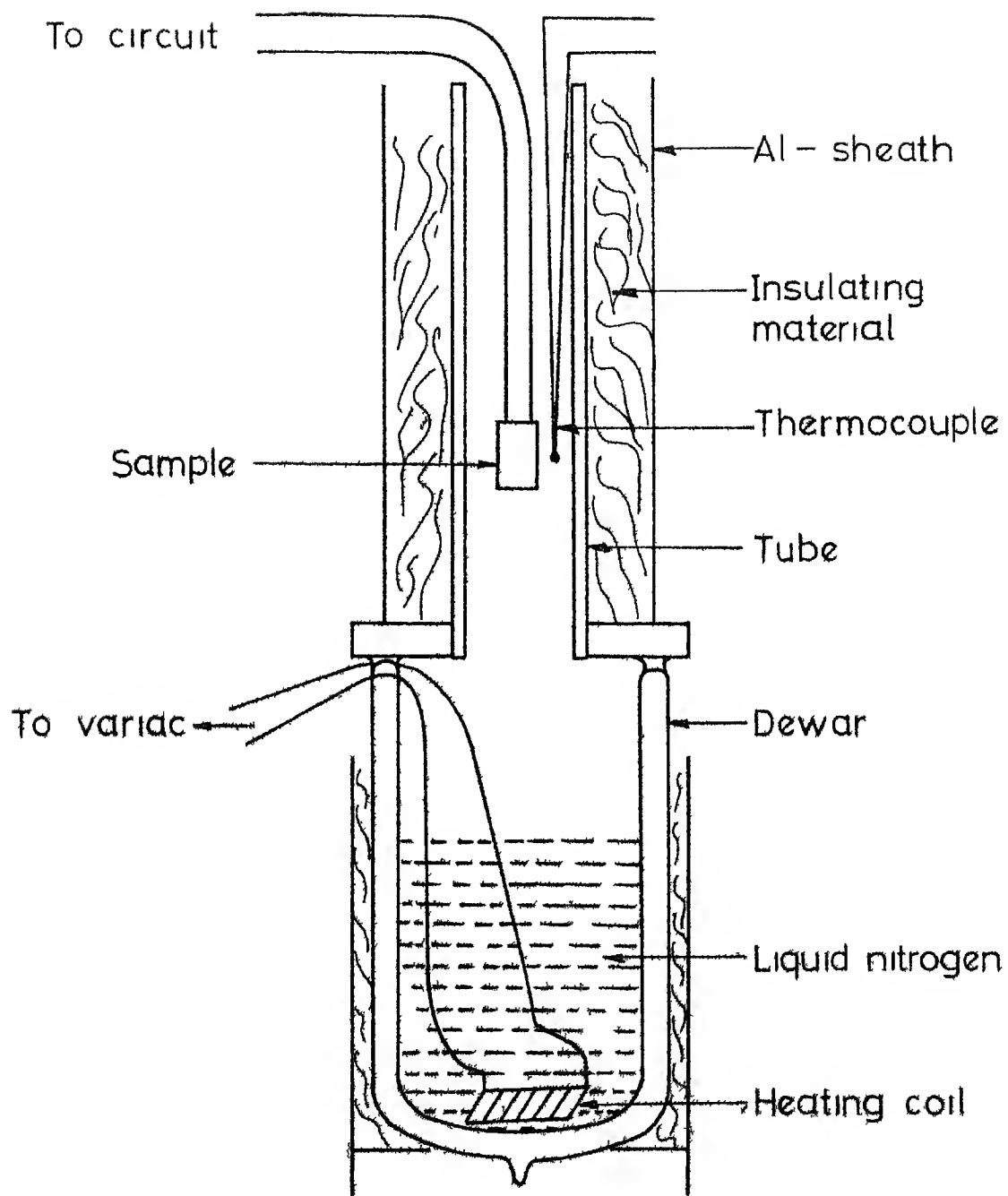


Fig 2 Setup of low temperature resistivity measurement

Temperatures were measured with the help of potentiometer and copper constant^{an} thermocouple

3 4 X-Ray Diffraction Measurements

Glasses were crushed and prepared in the fine powder form and sieved to get -400 mesh size powder. X-ray diffraction pattern was obtained with the help of a X-ray diffractometer in the range $2\theta = 10^\circ$ to $2\theta = 50^\circ$. This was done to assure that samples were in amorphous phase. Graphs does not indicate any detectable presence of crystalline phase.

3 5 Switching

Only one As_2O_3 containing glass no 14 showed the switching behaviour. The V-I characteristic curve for this glass was obtained at different temperature with the help of x-y recorder and resistance values were calculated from the slope in the linear region.

From resistance values the specific resistivity values were calculated. From log resistivity vs $\frac{1}{\text{Temperature}}$ plot activation energy values were obtained by calculating the slope by least squares method.

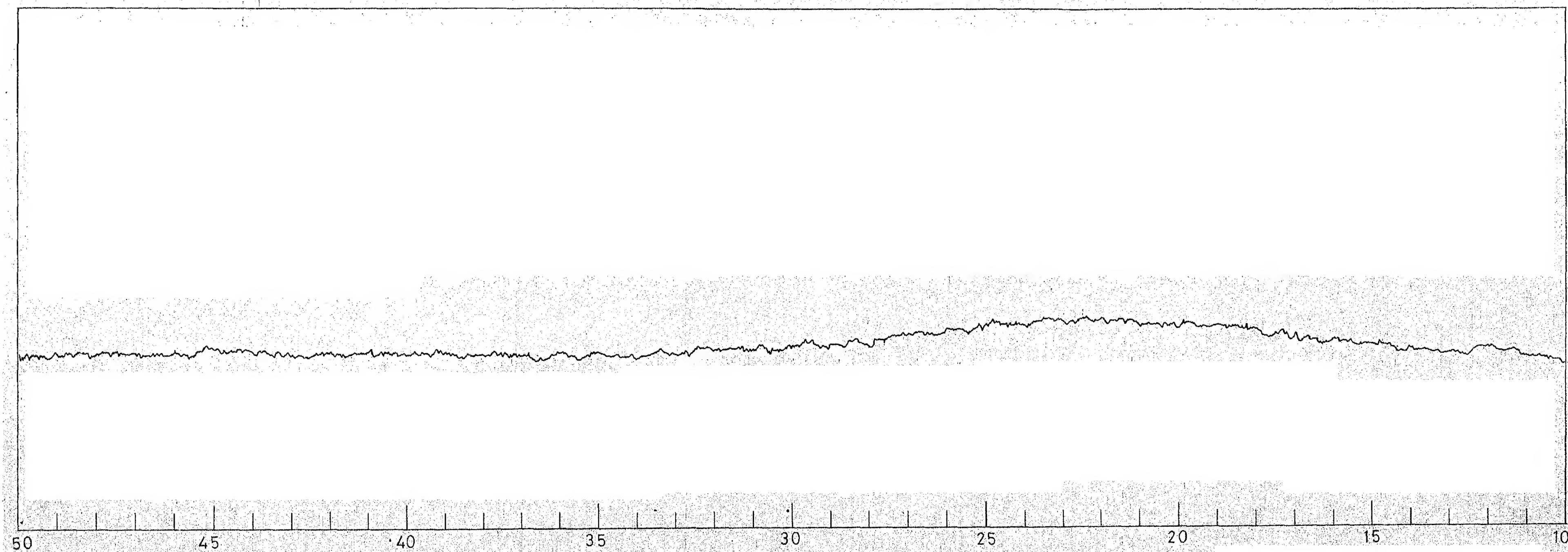


FIG.15 X-RAY DIFFERECTION PATTERN OF GLASS 5,9,13 &17

CHAPTER IV

RESULTS

4 1 Effect of Electrodes

Silver and gold electrodes were tried to determine the resistivity. Silver electrodes were made by painting silver paint⁽²⁴⁾ on both the sides of the samples while gold electrodes were made by vacuum deposition technique. It was seen that with silver electrodes the sample's current voltage characteristics were nonlinear and with gold electrodes the current voltage characteristic was linear. The I-V characteristics of glasses with silver and gold electrodes are shown in Fig. 3. Thus gold electrodes behave as ohmic contact between these glasses and gold.

4 2 Resistivity

The resistivity of the glasses can be given by

$$\rho = \rho_0 \exp \left(\frac{A}{kT} \right)$$

where ρ_0 and A are constants, A is called the activation energy. Therefore $\log \rho$ vs $1/T$ curve will be a straight line. There might be some deviation from this type of

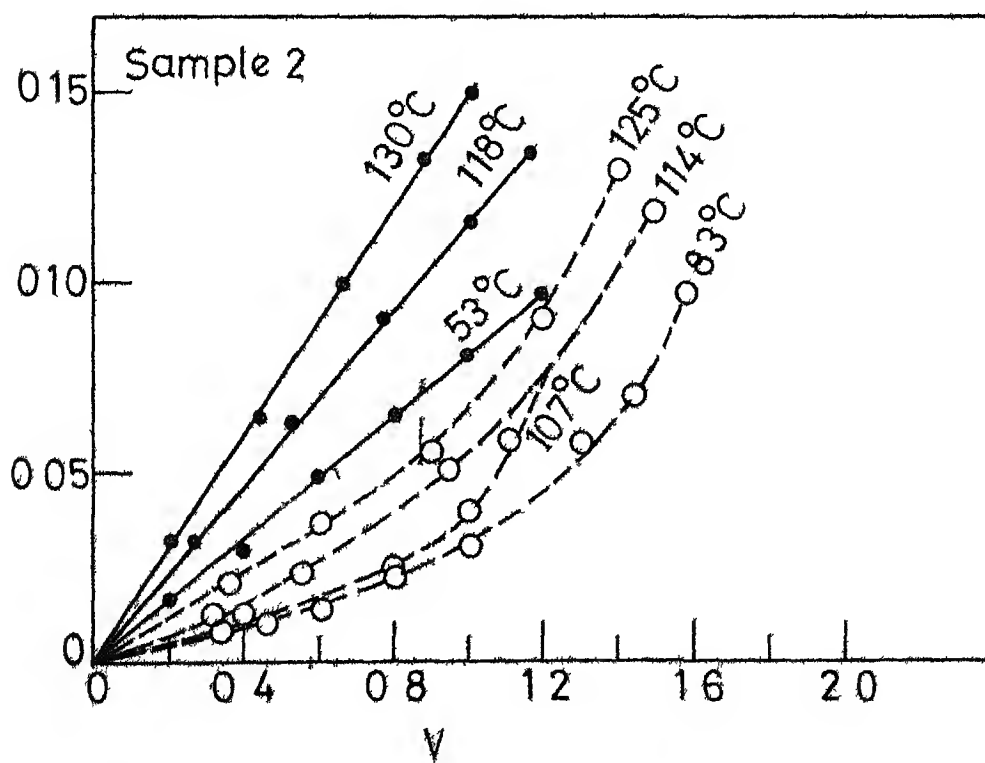
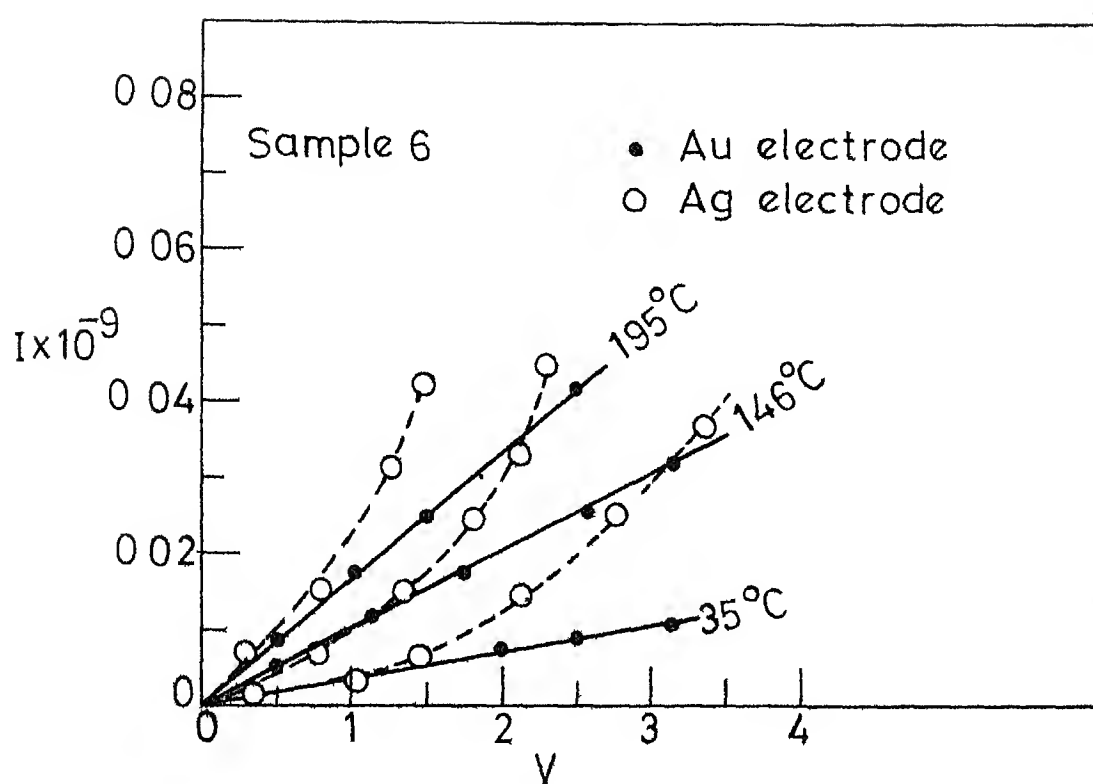


FIG. 3, V-I CHARACTERISTIC OF SILVER AND GOLD ELECTRODES

behaviour By plotting $\log \rho$ vs $1/T$ we can draw various inferences for the electrical conduction behaviour of the glass. All the glasses are grouped into eight groups accordingly to their composition, their logarithm resistivity with inverse of temperature are plotted in Figs 4-13.

GROUP I

The logarithm of resistivity as a function of inverse of temperatures for glasses 1, 2 and 3 are shown in Fig 4. In this group of glasses glass no 1 is the base glass of the system $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2$. In glass no 2 5 mole % Se is added and in glass no 3 5 mole / graphite is also added with 5 mole / Se. Fig 4 shows that as selenium is introduced the resistivity as well as activation energy decreases sharply. With the introduction of 5 mole / C (graphite) there is not much change in resistivity as well as in activation energy. The activation energies of these glasses are given in Table II as obtained using standard least squares method of fitting data. There was change in resistance level during heating and cooling cycles in glasses 1 & 3 while glass no 2 does not show any such change.

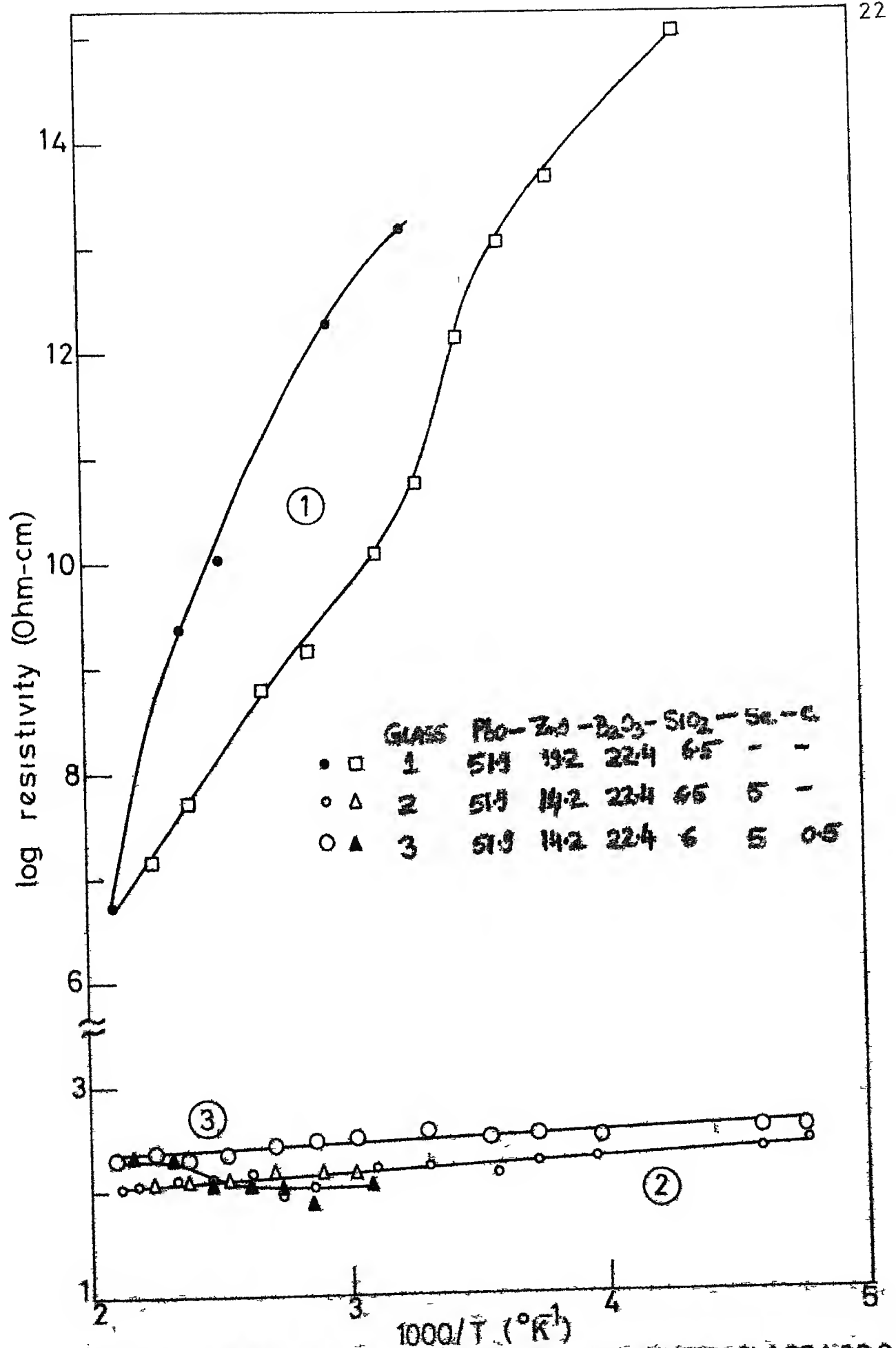


FIG. 4 VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 1, 2 & 3

GROUP II

In this group of glasses (glass no 4 & 5) the log resistivity vs $\frac{1}{T}$ curves are presented in Fig 5. The resistivity of glass 4 is 10^5 ohm cm at room temperature and increases with temperature. When content of B_2O_3 is increased from 12 mole / to 22 mole / and content of PbO-ZnO-Se are decreased in glass the resistivity falls by three orders of magnitude and also the trend of resistivity variation with temperature reversed i.e. the resistivity of glass no 5 decreases with increase in temperature. The activation energy of glass no 5 is given in Table II.

GROUP III

In group III which contains glass no 6, 7 & 8 only content of B_2O_3 and Se changes as given in the Fig 6 which also show resistivity behaviour of these glasses with temperature. In all the glasses resistivity values in heating cycles are not same as those of cooling cycle. All the glasses show similar behaviour with activation energy ranging between 7 to 10 eV.

GROUP IV

Figure 7 shows the effect of changing concentration of B_2O_3 and Se on the resistivity behaviour in

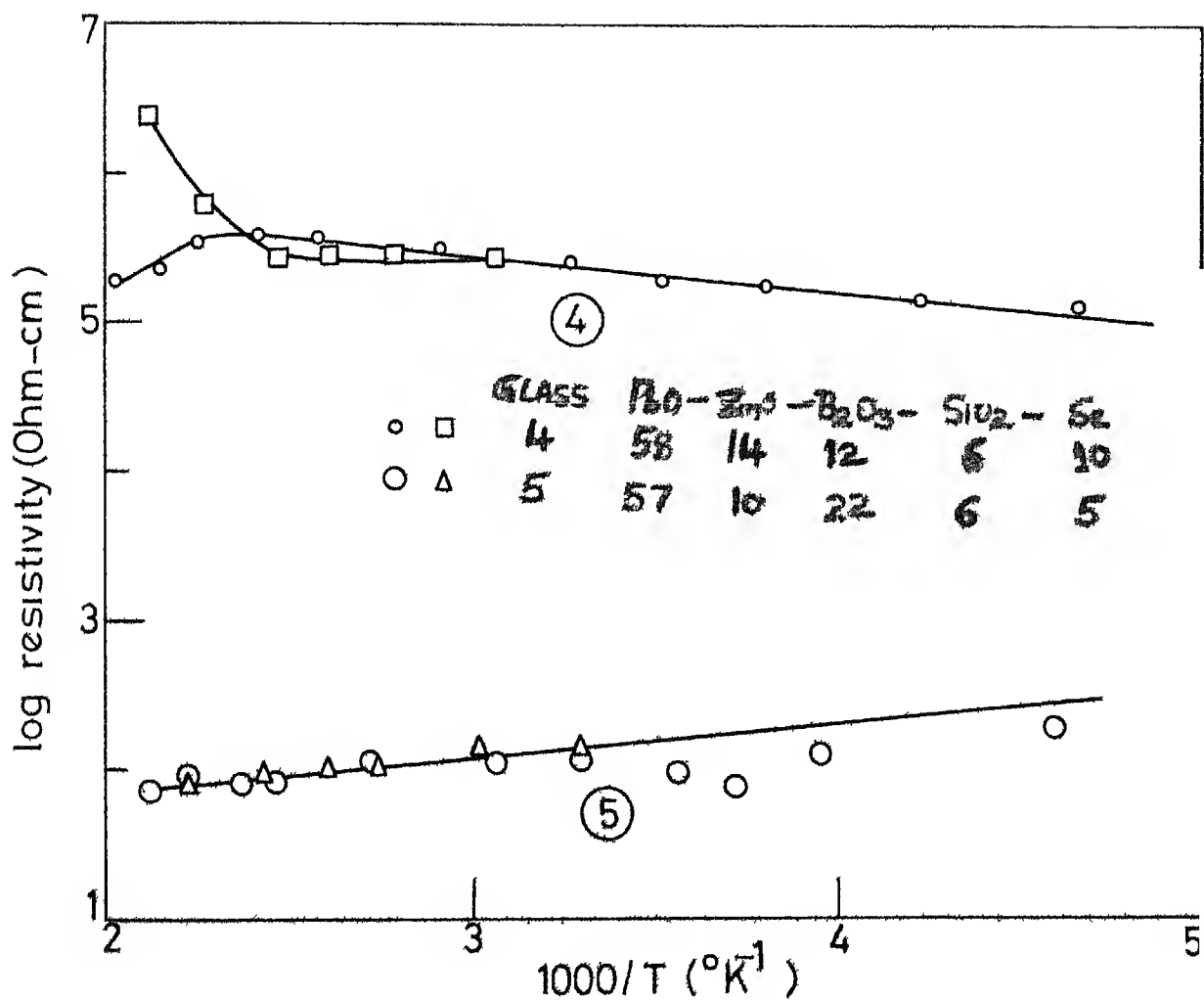


FIG 5 VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 4 & 5

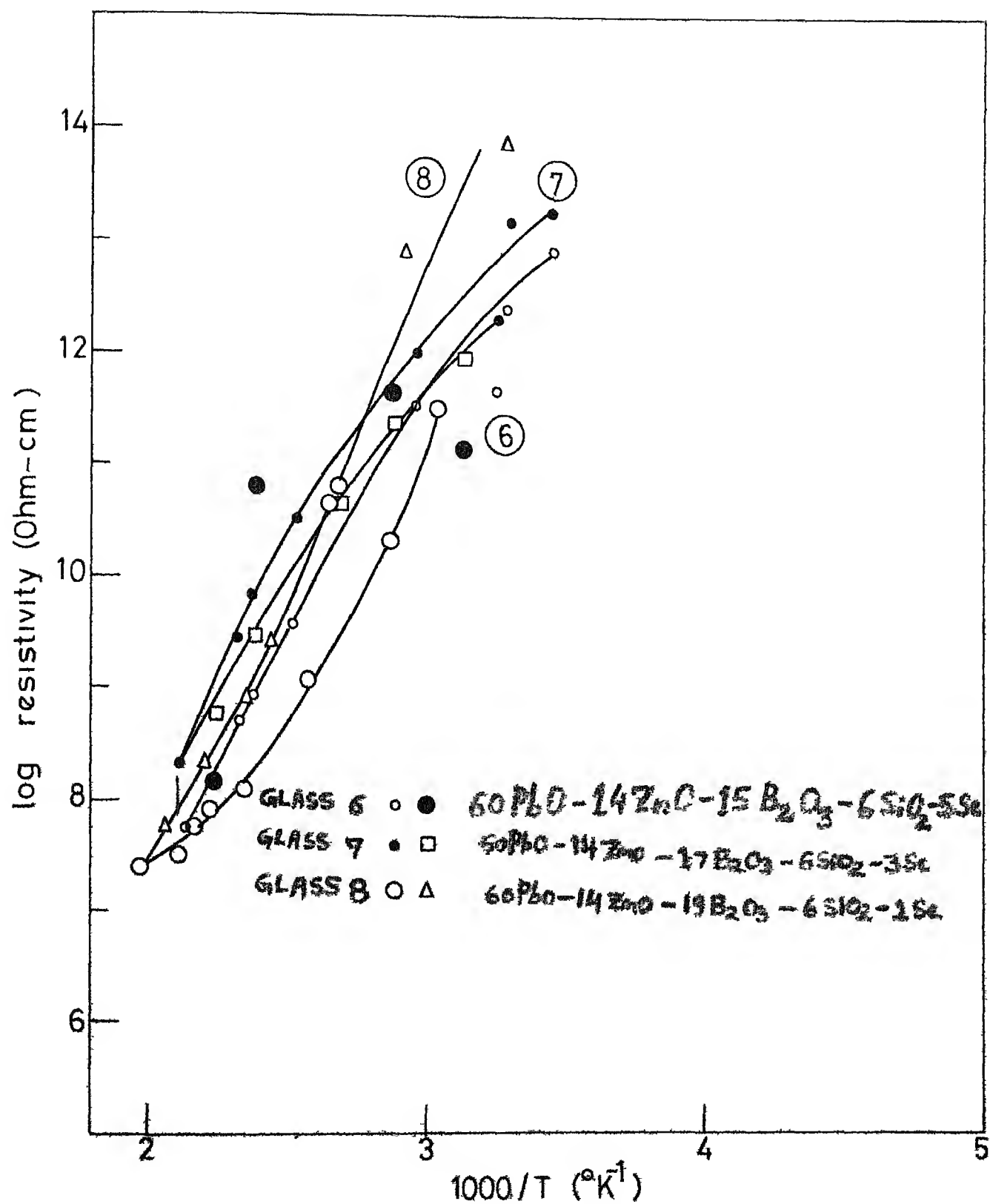


FIG 6 VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 6,7 & 8

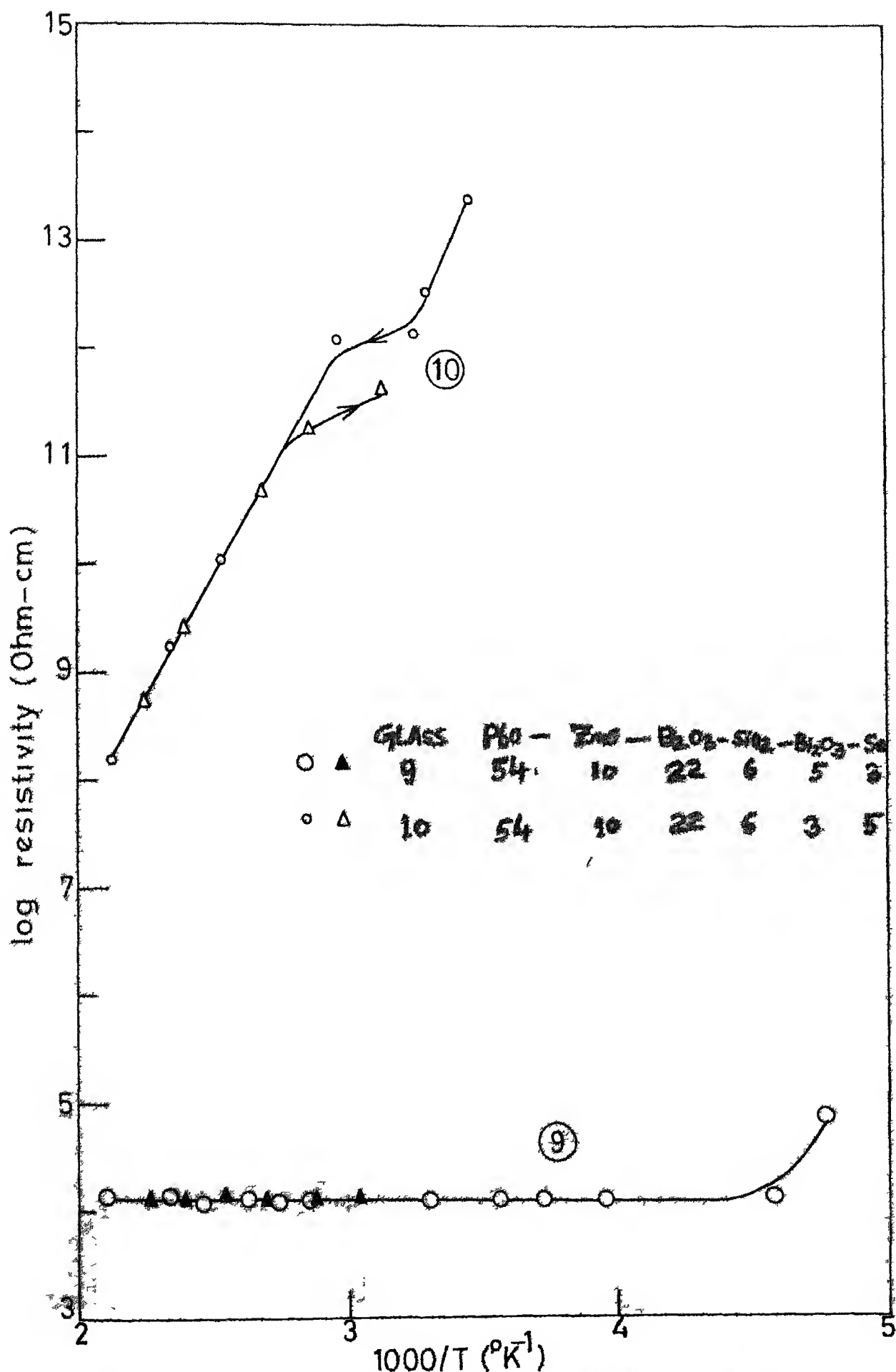


FIG 7 VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 9&10

glasses 9 and 10 The glass 9 having the composition $54\text{PbO}-10\text{ZnO}-22\text{B}_2\text{O}_3-6\text{SiO}_2-5\text{Bi}_2\text{O}_3-3\text{Se}$ has resistivity of the order of 10^{-4} ohm cm which is not affected by temperature At lower temperature however, there is some increase in resistivity

Glass 10 has a very high resistivity (10^{11} ohm cm at room temperature) in comparison to glass 9 Its resistivity decreases exponentially with temperature Resistivity values for heating and cooling cycles are almost same

GROUP V

Log resistivity vs $\frac{1}{\text{Temperature}}$ plots for the ¹²group are shown in Fig 8 In this group only antimony oxide and selenium content was varied

The resistivity of glass no 11 increases with increasing temperature during heating During cooling the resistivity further increases reaching a constant value near room temperature

The resistivity of glass 12 having 3% Sb_2O_3 and 5% Se is three orders of magnitude less than the resistivity of glass ¹²~~11~~ Its resistivity first decreases and then increases with temperature.

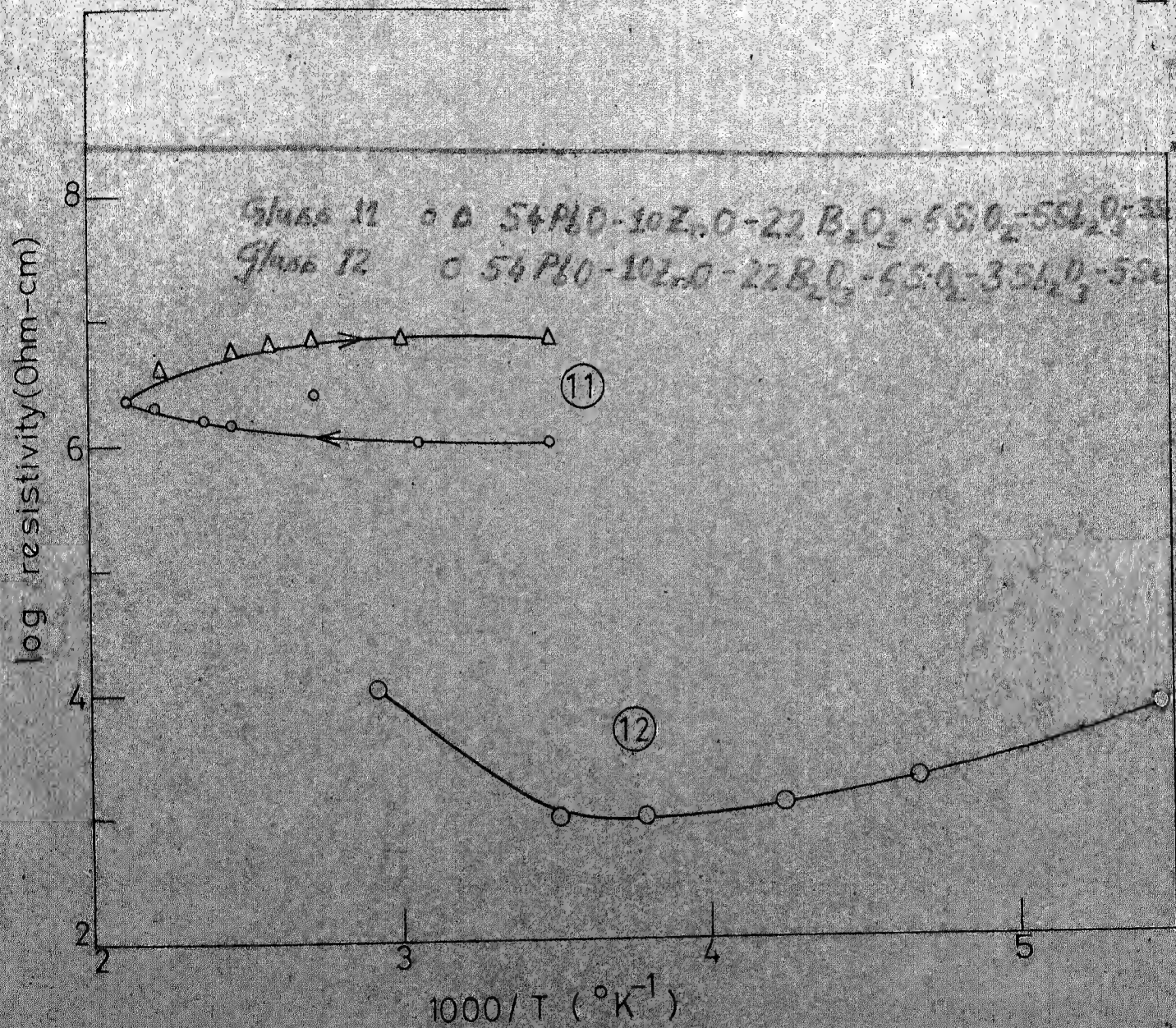


FIG. 8 VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 11 & 12

GROUP VI

The variation of resistivity with temperature of the glasses containing As_2O_3 are shown in Fig 9. Glass 13 containing $5\text{As}_2\text{O}_3-3\text{Se}$ has higher resistivity and activation energy than glass 14 containing $3\text{As}_2\text{O}_3-5\text{Se}$. This behaviour is reverse that of glasses 9 and 10 in which increase of Bi_2O_3 concentration leads to decrease in resistivity and activation energy.

In glass 13 resistivity values are higher for heating cycle than cooling cycle.

Fig 10 shows the relative variation of log resistivity with $1/\text{Temperature}$ for glasses 9, 11, 13. Glass 9 has the composition $54\text{PbO}-10\text{ZnO}-22\text{Bi}_2\text{O}_3-6\text{SiO}_2-3\text{Se}-5\text{Bi}_2\text{O}_3$. In glasses 11 and 13 Bi_2O_3 is replaced by Sb_2O_3 and As_2O_3 respectively. From Fig 10 it appears that glass 9 having Bi_2O_3 has lowest resistivity and is independent of temperature. Glass 11 containing Sb_2O_3 has two order higher resistivity than glass 9. The dependence of resistivity on temperature is again not much. Glass no 13 containing As_2O_3 has higher resistivity and activation energy.

Fig 11 shows the log resistivity vs $\frac{1}{T}$ for the same glass systems except having 3 mole % of Bi_2O_3 .

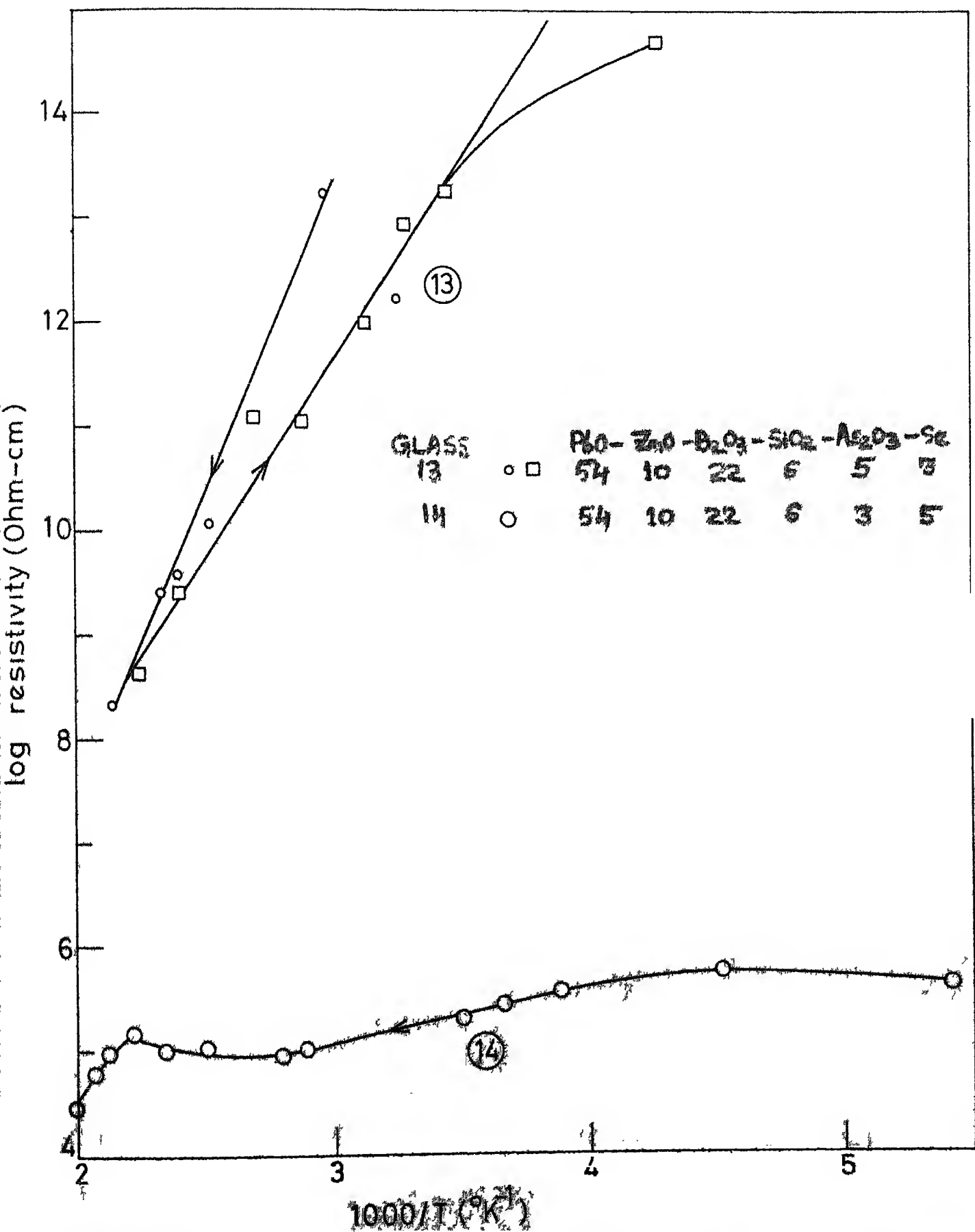


FIG. 9. VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 13 & 14

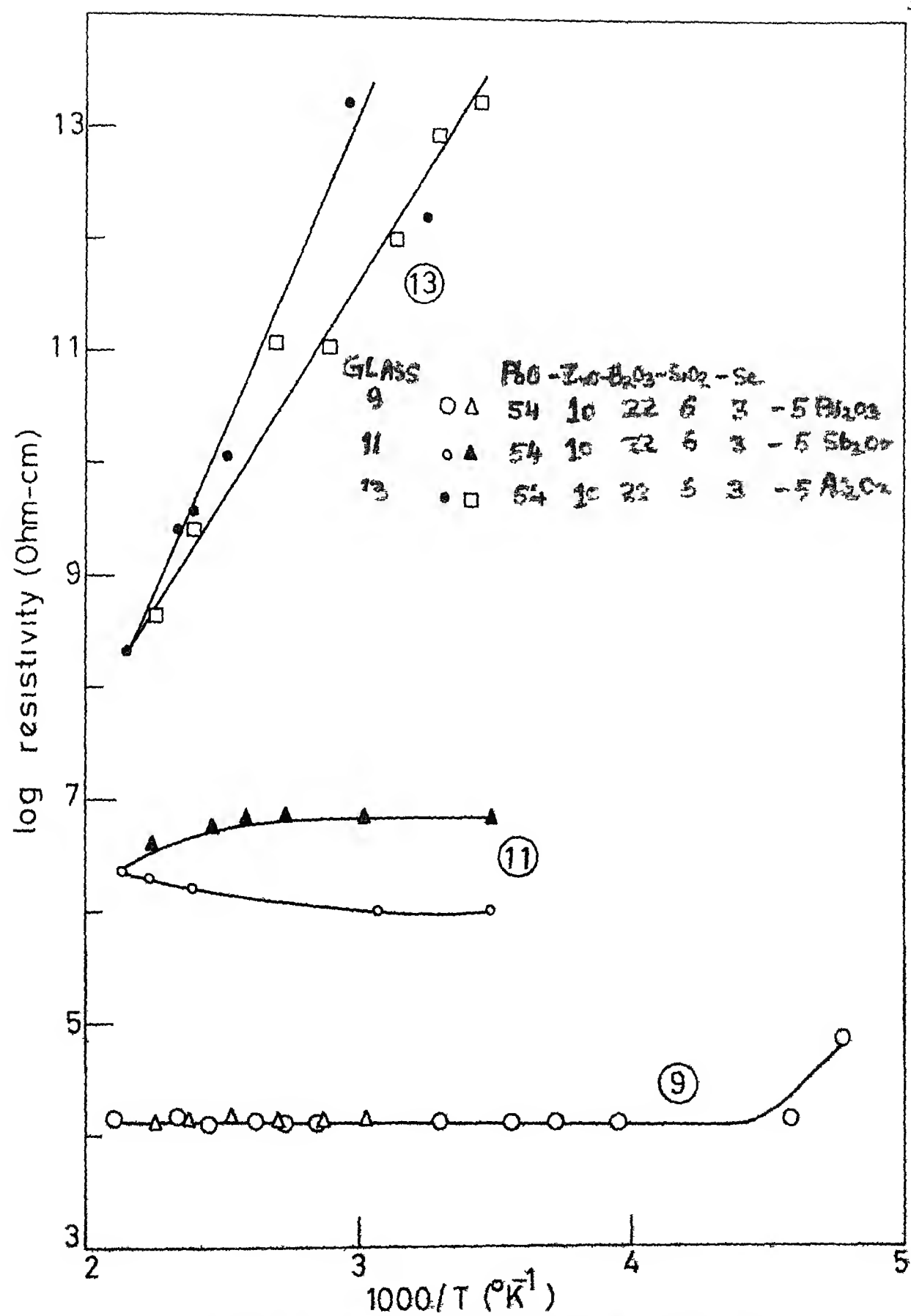


FIG 10 VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 9,11&13

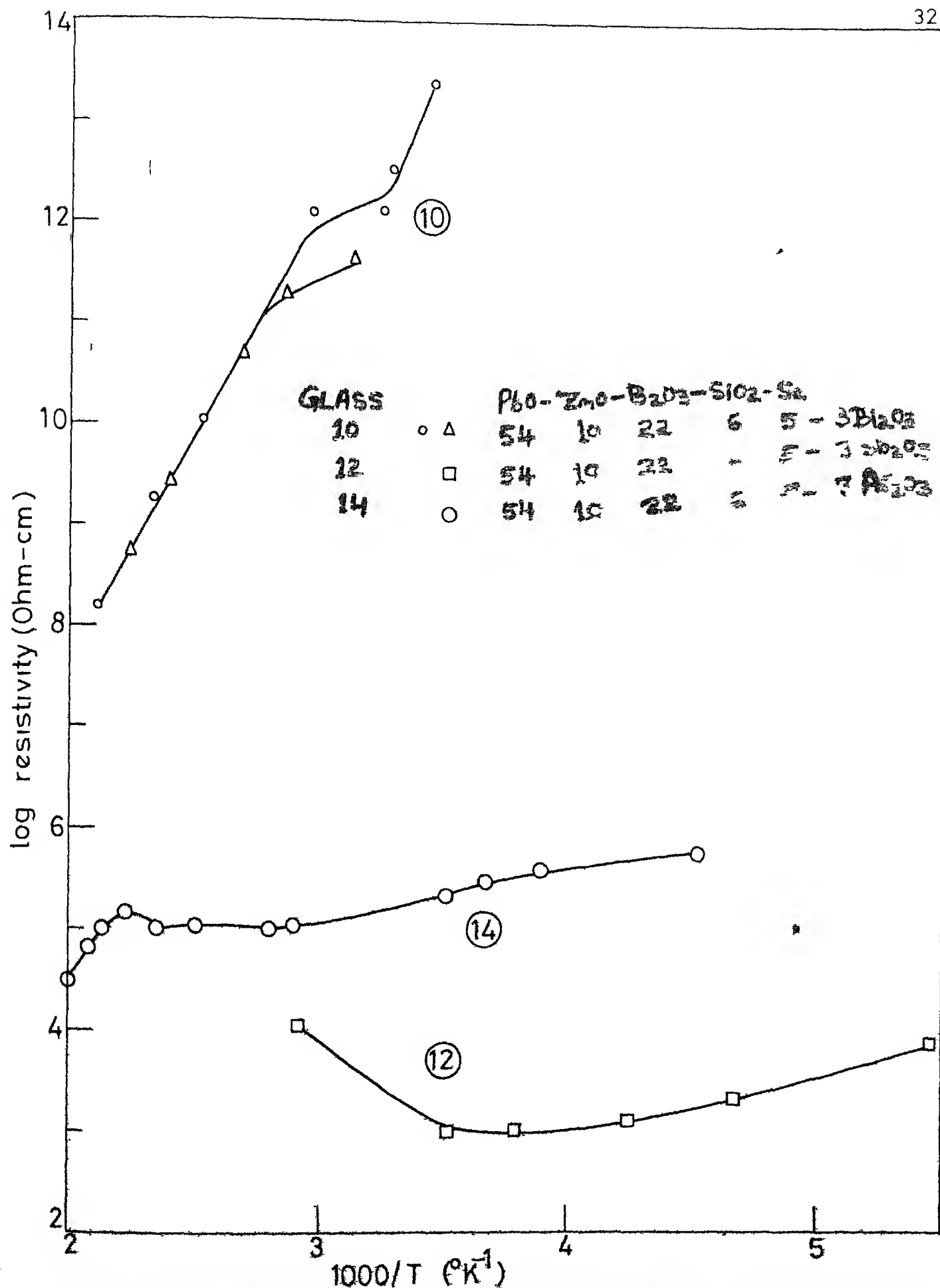


FIG. 11 VARIATION OF RESISTIVITY WITH $1/T$ FOR GLASS 10, 12 & 14

Sb_2O_3 & As_2O_3 respectively instead of 5 mole / and 5 mole % Se instead of 3 mole / In these glasses the behaviour is reversed, i.e. Ba_2O_3 containing glass (10) has highest resistivity and activation energy

Fig 12 & 13 presents the effect of changing PbO and SiO_2 composition in glasses containing Bi_2O_3 and Sb_2O_3 respectively Glass containing Bi_2O_3 shows lower resistivity value for higher mole / of PbO (glass no 15) In this glass the resistivity increases with increase in temperature Glass 16 has higher resistivity and activation energy

Glasses with antimony oxide have reversed behaviour, i.e. higher PbO containing glass shows higher resistivity In glass 18 during cooling resistivity suddenly increase by one order of magnitude and afterwards increase very slowly with decreasing temperature

4.3 Switching characteristics

Only one glass no 14 $54\text{PbO}-10\text{ZrO}-22\text{Bi}_2\text{O}_3-6\text{SiO}_2-3\text{As}_2\text{O}_3-5\text{Se}$ showed the threshold switching At 78°C with applied voltage of 3v resistance of sample dropped down from 10^5 to 3×10^3 Some typical voltage vs current plots are also presented in Fig 14 for different temperature.

A variation of threshold voltage and on' state resistants presented in Table III

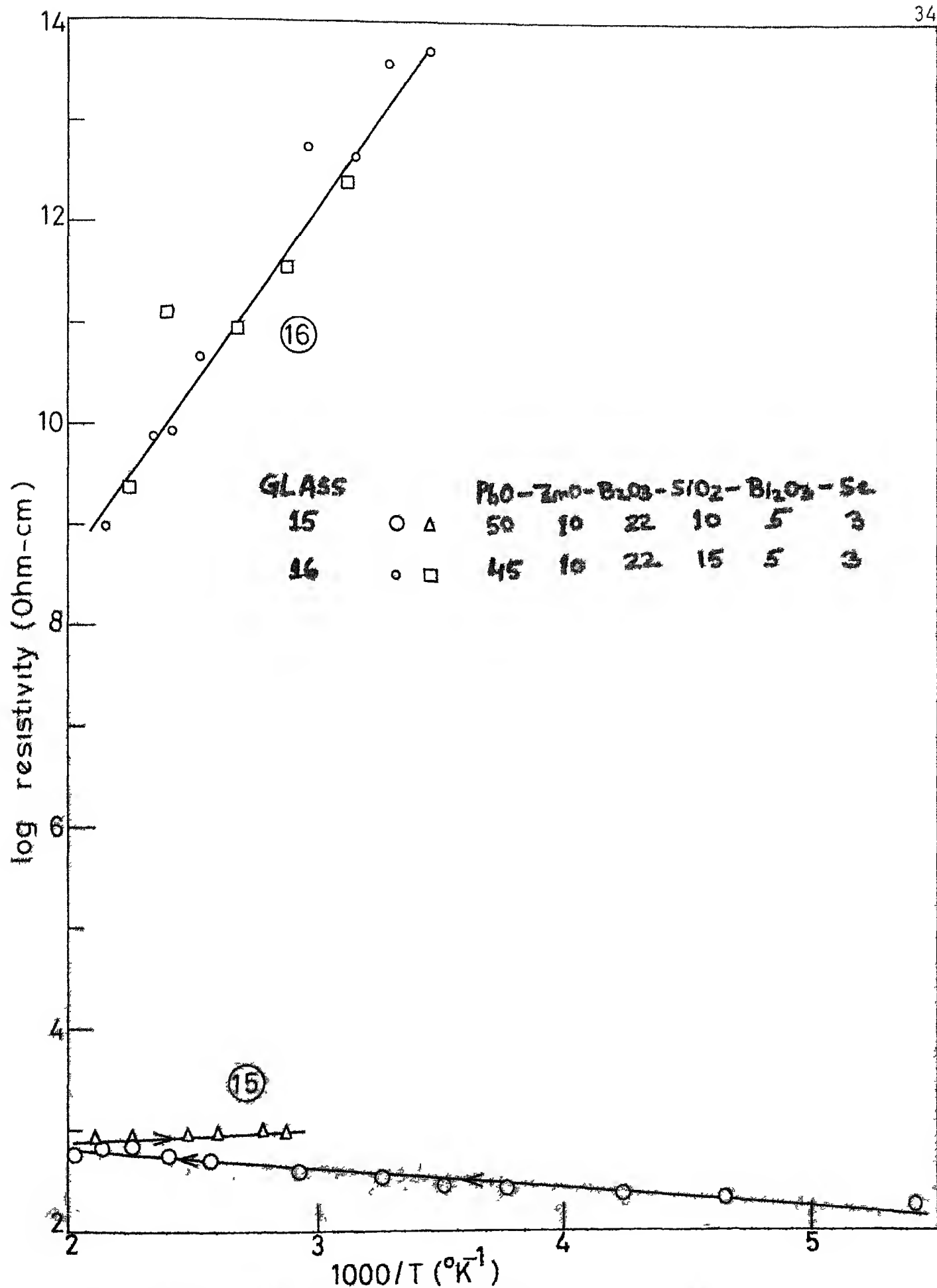


FIG 12, VARIATION OF RESISTIVITY WITH 1/T FOR GLASS 15 & 16

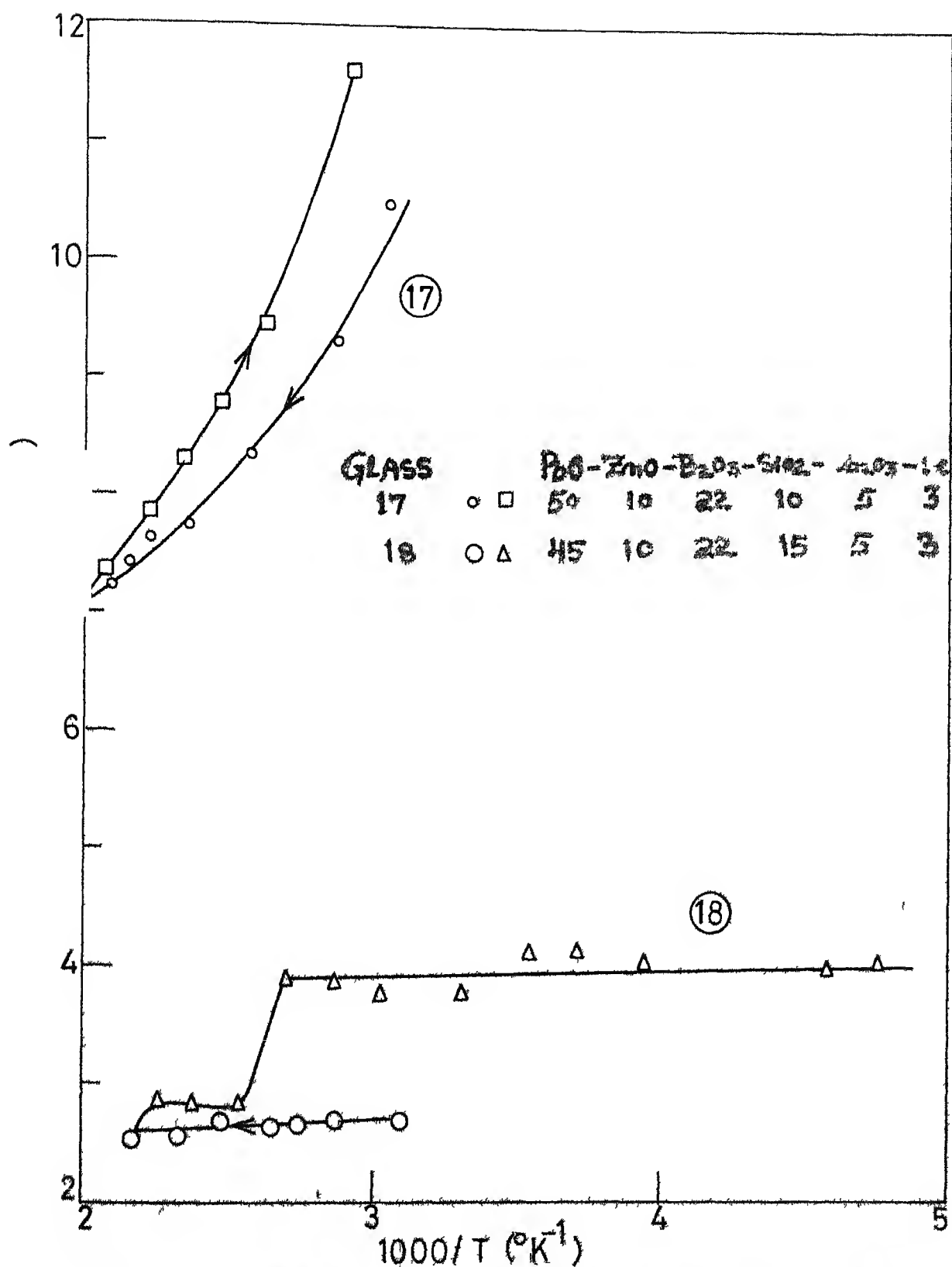


FIG 13 VARIATION OF RESISTIVITY WITH $1/T$ FOR GLASS 17 & 18

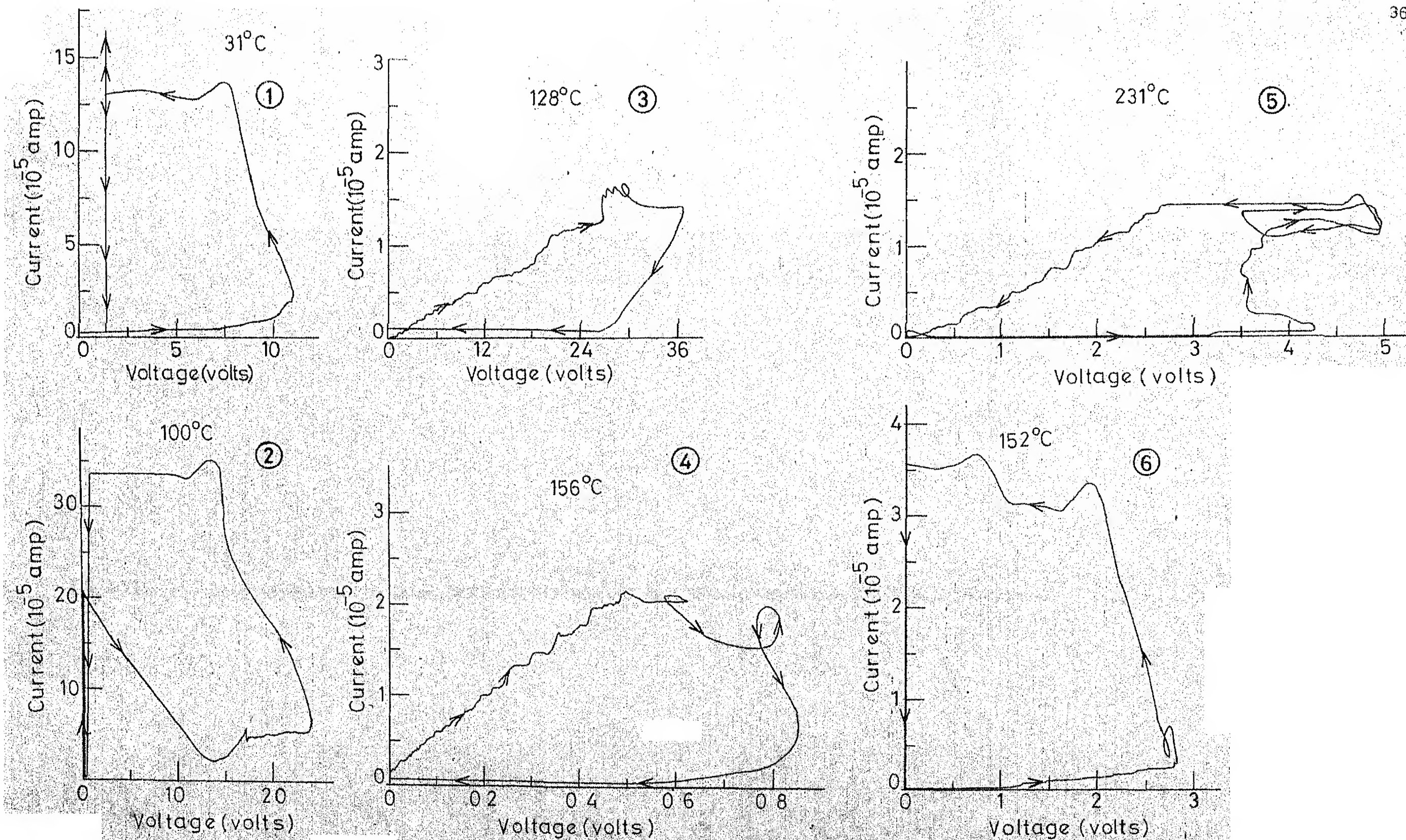


FIG. 14 V-I CHARACTERISTIC OF GLASS 14

TABLE 2

Activation energy data for glasses 6,8,13,16,17 & 18,
5.

Glass No	Activation Energy cv	Standard Deviation
6	0.7618	0361
8	0.9759	079
13	.61697	0301
16	.711	031
17	0.768	.0342
18	0.1419	022
5	0.755×10^{-2}	0.1871×10^{-2}

CHAPTER V

DISCUSSIONS

5.1 PbO-SiO₂ Glasses

The bulk resistivity of high lead containing glasses is 10^{16} ohm cm near room temperature as described by Morey⁽³⁷⁾ The resistivity of our base glass 51.9 PbO-19.2 ZnO, 22.4 B₂O₃ 6.5 SiO₂ (mole %) (Glass No 1) is of the order of 10^{12} ohm cm near room temperature. The decrease in resistivity may be due to addition of ZnO and B₂O₃. The $\log \rho$ vs $1/T$ curve is linear in agreement with the literature data. Addition of more PbO increases the resistivity since metallic ions added tend to fill up holes in the structure⁽²⁷⁾

5.2 Selenium

The resistivity of vitreous selenium is 10^{13} ohm cm⁽²⁸⁾ and of liquid selenium is 1.3×10^5 ohm-cm⁽²⁹⁾ (400°C)

By substitution of 5% Se for ZnO to the base glass decrease the resistivity from 10^{12} ohm cm to 10^2 ohm-cm (Fig. 1). By substituting of Se for B₂O₃ in the glasses there is not much change in resistivity (Fig. 3)

5.3 Electronic Conduction

Microstructural studies of silicate glasses containing Bi_2O_3 by Chakravorty⁽³⁸⁾ shows there are islands of Bi in the glassy matrix of varying diameters 250 Å. One possibility for conduction arise from hopping between conducting islands. Se droplets may also be present in glassy matrix as suggested by Nagesh⁽³⁹⁾. Thus conduction may arise from the hopping between the conducting islands of Bi and Se. The resistivity of these glasses can be represented by

$$\rho = \rho_0 \exp (A/kT)$$

The activation energy for electron hopping in such a situation has been shown by Neubauer and Wibb⁽⁴⁰⁾ to be given by e^2/kr , where e is the electronic charge, k is the dielectric constant of the glassy matrix and r is the diameter of the conducting island. The resistivity of such glasses should be higher than the resistivity of Bi, Sb and Se. We see some glasses have high value of resistivity i.e. of the order of $10^9 - 10^{12}$ ohm-cm at room temperature, while some glasses show very low value of resistivity ($10^2 - 10^5$ ohm-cm). The resistivity behaviour

of high resistivity glasses can be described as above

The dielectric constants of lead glasses is 9⁽³⁷⁾

Using above formula with activation energy values ranging from 7 to 10 eV a range of $\frac{h}{kT}$ values extending from 10 $\frac{h}{kT}$ to 30 $\frac{h}{kT}$ are obtained. The droplets of this size can not be detected from X-ray diffraction patterns which shows no peak and conforms suggests glassy structure. For conformation of this size of droplets needs electron microscopic studies of these glasses.

We see from Figs (1-10) except Fig 2 that by changing the composition of the glasses by varying concentration of Se, Bi_2O_3 , Sb_2O_3 and As_2O_3 , the resistivity value, drop from a very high value to a low values and also the variation of resistivity with temperature is also very small. In some cases the (Glass Nos 4 and 15) the resistivity increases with increase in temperature similar to the case in metals.

The phenomenon seems to arise due to Anderson transition⁽³⁴⁾ and can be explained on the basis of Anderson localization theorem⁽³³⁾

Change of the concentration of different components of the glass changes the structure in such a manner that the Fermi level shifts from region localized states towards the region of extended states. The conduction from hopping between the localized states changes to either conduction due to excitation of electrons to the extended states, where activation energy will be low and decreases with increase in temperature or Fermi level reaches the region of extended states and electron becomes itinerant and behaves like a metal. In this case the conductivity is high.

CHAPTER VI

CONCLUSIONS

Glasses in the system $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2$ showed high value of resistance which is in agreement with the literature data. When Se metal was substituted in ^{place} phase of ZnO in the glass system there was a remarkable change in the resistivity level of these glasses. Substitution of Se for B_2O_3 in the glass does not show much change in resistivity. Variation of composition of Bi_2O_3 , Sb_2O_3 and As_2O_3 gave rise to different level of resistivity level. Some of the log resistivity vs temperature curves are linear and showed much variation of resistivity with temperature. While for others the variation was very small.

Conduction in these glasses at low temperatures seems to arise due to electrode ⁿ hopping between conducting island formed in the glassy matrix.

By increasing the concentration of PbO lead to increase in resistivity which can be explained on the basis that big Pb^{2+} ions tend to fill up the holes and thus decrease the electric conduction. Increase in SiO_2 content leads to increase in resistivity because the structure becomes more rigid. One As_2O_3 containing

glass also showed threshold switching

Thus by playing with the composition of different constituents of the glasses a variation of resistivity level from 10^{12} to 10^2 was obtained. X-Ray diffraction pattern took for different glasses does not show any peak hence indicated that crystalline particle will be smaller in size to be detected by this technique

A more extensive composition variation effect, microstructure studies D T A studies a c resistivity and dielectric constant measurements should be done before we could conclude on exact mode of conduction

Preposed Future Work

- 1 ^{Many} ~~Men~~ extensive composition variation studies in each individual system
- 2 A C resistance variation with temperature and dielectric properties measurements
- 3 D T A studies for these glasses
- 4 Microstructural studies like variation of electrical properties with microstructural variation

APPENDIX

TABLE 3

Resistivity Data of Glass No 1

51 9PbO-19 2ZnO-22 4B₂O₃-6 5 SiO₂ (Mole %)

Thickness of the specimen = 0.056 Cm

Area of the electrode = 2.15 Cm²

Temperature °K	Resistance ohm	Resistivity ohm-cm
308	3.87×10^{11}	1.49×10^{13}
338	4.86×10^{10}	1.87×10^{12}
394	2.8×10^8	1.07×10^{10}
424	5.63×10^7	2.16×10^9
429	5.43×10^7	2.08×10^9
475	1.3×10^5	4.99×10^6
447	3.75×10^5	1.44×10^7
418	1.3×10^6	4.99×10^7
373	1.55×10^7	5.95×10^8
350	3.7×10^7	1.42×10^9
319	3×10^8	1.15×10^{10}
304	1.59×10^9	6.10×10^{10}
290	3.79×10^{10}	1.46×10^{12}
217	3.1×10^{11}	1.19×10^{13}
262	1.2×10^{12}	4.61×10^{13}
232	3×10^{13}	1.15×10^{15}

TABLE 4

Resistivity Data of Glass No 2

51 9PbO-14 2ZnO-22 4B₂O₃-6 5SiO₂-5Se (Mole/)

Thickness of the specimen = 0.07 cm

Area of the electrode = 1.63 cm²

Temperature °K	Resistance Ohms	Resistivity Ohm-cm
210	12.5	2.91×10^2
218	9.64	2.24×10^2
253	8.46	1.97×10^2
269	8.0	1.86×10^2
281	6.15	1.43×10^2
303	7.33	1.71×10^2
323	7.14	1.66×10^2
351	4.64	1.08×10^2
365	4.23	9.8×10^1
382	6.43	1.49×10^2
405	5.5	1.28×10^2
429	5.62	1.31×10^2
460	5.0	1.16×10^2
475	4.37	1.02×10^2
445	5.5	1.28×10^2
420	5.55	1.29×10^2
395	5.55	1.29×10^2
370	6.47	1.51×10^2
348	6.28	1.46×10^2
330	5.83	1.36×10^2

TABLE 5

Resistivity Data of Glass No 3

51 9PbO-14 2ZnO-22 4R₂O₃-6SiO₂-5Se-O 5C(Mole/)

Thickness of the specimen = 0.05 Cm

Area of the electrode = 0.45 Cm²

Temperature °K	Resistance Ohms	Resistivity Ohm-cm
210	3.75x10	3.38x10 ²
218	4.0x10	3.6x10 ²
253	3.89x10	3.5x10 ²
269	3.65x10	3.29x10 ²
281	3.44x10	3.096x10 ²
303	3.89x10	3.5x10 ²
330	3.57x10	3.21x10 ²
348	3.39x10 ¹	3.05x10 ²
370	3.103x10 ¹	2.79x10 ²
395	2.5x10 ¹	2.25x10 ²
420	2.22x10 ¹	1.998x10 ²
445	2.67x10 ¹	2.4x10 ²
475	2.3x10 ¹	2.07x10 ²
460	2.25x10 ¹	2.025x10 ²
429	2.17x10 ¹	1.95x10 ²
405	1.29x10 ¹	1.16x10 ²
382	1.25x10 ¹	1.125x10 ²
365	1.2x10 ¹	1.08x10 ²
351	7.86	7.07x10 ¹
323	1.78x10 ¹	1.15x10 ²

TABLE 6

Resistivity Data of Glass No 4

58PbO-14ZnO-12B₂O₃-6SiO₂-10Se (Molc)

Thickness of the specimen = 0.063 Cm

Area of the electrode = 7.89 Cm²

Temperature, °K	Resistance Ohms	Resistivity Ohm-cm
183	2.46×10^3	1.13×10^5
215	2.813×10^3	1.29×10^5
237	3.125×10^3	1.43×10^5
363	2.8×10^3	1.74×10^5
285	4.06×10^3	1.86×10^5
307	5.44×10^3	2.5×10^5
343	6.84×10^3	3.14×10^5
389	8.235×10^3	3.78×10^5
417	8.076×10^3	3.7×10^5
445	7.22×10^3	3.31×10^5
467	5×10^3	2.29×10^5
495	4.09×10^3	1.88×10^5
474	5.28×10^4	2.42×10^6
442	1.36×10^4	6.24×10^5
406	5.77×10^3	2.65×10^5
385	6.09×10^3	2.79×10^5
359	6.25×10^3	2.87×10^5
327	6.29×10^3	2.89×10^5

TABLE 7

Resistivity Data of Glass No.5

57PbO-10ZnO-22B₂O₃-6SiO₂-5 Se (Mole /)

Thickness of the specimen = 0.055 cm

Area of the electrode = 1.33 cm²

Temperature °K	Resistance Ohms	Resistivity Ohm-cm
210	1.33x10 ¹	3.22x10 ²
218	8.0	1.93x10 ²
253	5.18	1.25x10 ²
269	3.14	7.59x10 ¹
281	4.0	9.67x10 ¹
304	5.14	1.24x10 ²
327	4.57	1.11x10 ²
367	4.67	1.13x10 ²
406	3.54	8.56x10 ¹
422	3.43	8.29x10 ¹
451	3.37	8.15x10 ¹
472	3.00	7.25x10 ¹
491	3.47	8.39x10 ¹
410	3.89	9.41x10 ¹
385	4	9.67x10 ¹
365	4.38	1.06x10 ²
332	5.8	1.40x10 ²
304	6	1.45x10 ²

TABLE 8

Resistivity Data of Glass No 6

 $60\text{PbO}-14\text{ZnO}-15\text{B}_2\text{O}_3-6\text{SiO}_2-5\text{Se}$ (Mole %)

Thickness of the specimen = 0.051 Cm

Area of the electrode = 0.45 Cm^2

Temperature, $^{\circ}\text{K}$	Resistance, Ohms	Resistivity, Ohm Cm
290	9.0×10^{11}	7.94×10^{12}
304	2.5×10^{11}	2.21×10^{12}
308	5.0×10^{10}	4.41×10^{11}
338	3.63×10^{10}	3.25×10^{11}
397	4.43×10^8	3.91×10^9
419	1×10^8	8.82×10^8
429	5.59×10^7	4.93×10^8
468	6.52×10^6	5.75×10^7
447	1.64×10^7	1.45×10^8
419	6.92×10^9	6.11×10^{10}
373	6.92×10^9	6.11×10^{11}
349	4.69×10^{10}	4.14×10^{11}
319	1.64×10^{10}	1.45×10^{11}

TABLE 9

Resistivity Data of Glass No 7

 $60\text{PbO}-14\text{ZnO}-17\text{B}_2\text{O}_3-6\text{SiO}_2-3\text{Se}$ (Mole %)

Thickness of the specimen = 0.031 Cm

Area of the electrode = 0.50 Cm^2

Temperature $^{\circ}\text{K}$	Resistance Ohm	Resistivity Ohm-cm
290	1.09×10^{12}	1.76×10^{13}
304	9.5×10^{11}	1.53×10^{13}
308	1.25×10^{11}	2.02×10^{12}
338	6.05×10^{10}	9.76×10^{11}
396	1.92×10^9	3.10×10^{10}
424	3.85×10^8	6.21×10^9
429	1.67×10^8	2.69×10^9
473	1.28×10^7	2.06×10^8
497	3.57×10^7	5.76×10^8
518	1.66×10^8	2.68×10^9
573	2.76×10^9	4.45×10^{10}
650	1.42×10^{10}	2.29×10^{11}
719	5.74×10^{10}	9.26×10^{11}

TABLE 10

Resistivity Data of Glass No 8

 $60\text{PbO}-14\text{ZnO}-19\text{B}_2\text{O}_3-6\text{SiO}_2-1\text{Se}$ (Mole %)

Thickness of the specimen = 0.031 cm

Area of the electrode = 0.42 cm²

Temperature °K	Resistance Ohms	Resistivity Ohm-cm
329	2.5×10^{10}	3.09×10^{11}
348	1.62×10^9	2.00×10^{10}
387	9.57×10^7	1.18×10^9
425	9.80×10^6	1.21×10^8
450	6.41×10^6	7.91×10^7
453	6.25×10^6	7.72×10^7
463	4.69×10^6	5.79×10^7
474	2.5×10^6	3.09×10^7
508	2.0×10^6	2.47×10^7
182	4.55×10^6	5.62×10^7
454	1.67×10^7	2.06×10^8
429	6.52×10^7	8.05×10^8
409	2.14×10^8	2.64×10^9
377	3.46×10^9	4.27×10^{10}
347	6.25×10^{11}	7.72×10^{12}
304	5.88×10^{12}	7.26×10^{13}

TABLE 11

Resistivity Data on Glass No. 9

 $54\text{PrO}-10\text{ZnO}-22\text{B}_2\text{O}_3-6\text{SiO}_2-5\text{Ba}_2\text{O}_3-3\text{Se}$ (Mole %)

Thickness of the specimen = 0.047 cm

Area of the electrode = 0.5 cm²

Temperature, °K	Resistance, Ohms	Resistivity, Ohm-cm
210	6.65×10^3	7.04×10^4
218	1.19×10^3	1.27×10^4
253	1.19×10^3	1.27×10^4
269	1.19×10^3	1.27×10^4
281	1.19×10^3	1.27×10^4
303	1.19×10^3	1.27×10^4
323	7.69×10^3	8.18×10^4
351	1.21×10^3	1.29×10^4
365	1.14×10^3	1.21×10^4
382	1.25×10^3	1.33×10^4
405	1.1×10^3	1.17×10^4
429	1.34×10^3	1.43×10^4
475	1.30×10^3	1.38×10^4
445	1.19×10^3	1.27×10^4
470	1.25×10^3	1.33×10^4
395	1.335×10^3	1.42×10^4
370	1.19×10^3	1.27×10^4
348	1.19×10^3	1.27×10^4
330	1.275×10^3	1.36×10^4

TABLE 12

Resistivity Data of Class No 10

54Pbo-10Zno-22B₂O₃-6Sio₂-3B₁O₃-5Se (Mole %)

Thickness of the specimen = 0.062 cm

Area of the electrode = 1.70 cm²

Temperature, °K	Resistance, Ohms	Resistivity, Ohm cm
233	3.0×10^{13}	8.23×10^{14}
290	8.75×10^{11}	2.40×10^{13}
304	1.24×10^{11}	3.40×10^{12}
308	1.0×10^{10}	1.37×10^{12}
338	4.55×10^{10}	1.25×10^{12}
397	4.04×10^8	1.11×10^{10}
421	9.20×10^7	2.52×10^9
429	6.43×10^7	1.76×10^9
473	5.23×10^6	1.3×10^8
447	1.79×10^7	4.91×10^8
418	9.56×10^7	2.62×10^9
373	1.67×10^9	4.58×10^{10}
350	6.67×10^9	1.83×10^{11}
319	1.47×10^{10}	4.03×10^{11}

TABLE 13

Resistivity Data of Glass No 11

54Pbo-10Zno-22B₂O₃-6Sio₂-5Sb₂O₃-3Se (Mole /)

Thickness of the specimen =0.091 cm

Area of the electrode =3.0cm²

Temperature, °K	Resistance, Ohms	Resistivity ohm cm
304	3.18×10^4	1.05×10^6
327	3.18×10^4	1.05×10^6
366	7.9×10^4	2.60×10^6
406	4.4×10^4	1.45×10^6
422	5.0×10^4	1.65×10^6
451	6.3×10^4	2.08×10^6
471	7.0×10^4	2.31×10^6
448	1.25×10^5	4.12×10^6
408	1.79×10^5	5.90×10^6
387	2.07×10^5	6.82×10^6
367	2.08×10^5	6.86×10^6
332	2.20×10^5	7.25×10^6
304	2.13×10^5	7.02×10^6

TABLE 14

Resistivity Data of Glass No 12

54Pbo-10Zno-22B₂O₃-6Sio₂-3Sb₂O₃-5Se (mole /)

Thickness of the specimen =0.058 cm.

Area of the lelectrode =1.68 cm²

Temperature, °K	Resistance ohm	Resistivity ohm cm
183	2.5×10^2	7.24×10^3
215	6.67×10^1	1.93×10^3
237	4.2×10^1	1.22×10^3
264	3.53×10^1	1.02×10^3
285	3.41×10^1	9.88×10^3
307	1.05×10^3	3.04×10^4
343	4.0×10^2	1.16×10^4

TABLE 15

Resistivity Data of Glass No 13

54Pbo-10Zno-22B₂O₃-6Sio₂-5As₂O₃-3Se(Mole %)

Thickness of the specimen=0.09 cm

Area of the electrode = 1.5 cm²

Temperature, °K	Resistance, ohms	Resistivity, ohm.cm
308	1.00×10^{11}	1.67×10^{12}
338	1×10^{12}	1.67×10^{13}
398	7.29×10^8	1.21×10^{10}
419	2.212×10^8	3.69×10^9
429	1.46×10^8	2.43×10^9
468	1.27×10^7	2.12×10^8
447	2.78×10^7	4.62×10^8
418	4.43×10^8	2.38×10^9
373	7.29×10^9	1.21×10^{11}
350	6.78×10^9	1.13×10^{11}
319	6.1×10^{10}	1.02×10^{12}
304	5.51×10^{11}	9.18×10^{12}
290	1.09×10^{12}	1.81×10^{13}
233	2.99×10^{13}	4.98×10^{14}

TABLE 16

Resistivity Data of Glass No 11

54Pbo-10Zno-22B₂O₃-6SiO₂-3As₂O₃-5Se (Mole %)

Thickness of the specimen = 0.05 cm.

Area of the electrode = 0.24 cm²

Temperature, °K	Resistivity ohm cm
185	4.05x10 ⁵
221	5.63x10 ⁵
238	1.25x10 ⁷
257	3.6 x10 ⁵
273	2.84x10 ⁵
286	2.04x10 ⁵
317	1.0 x10 ⁵
359	9.25x10 ⁴
401	1.08x10 ⁵
429	1.008x10 ⁵
452	1.404x10 ⁵
471	9.792x10 ⁴
485	5.76x10 ⁴
504	2.88x10 ⁴

TABLE 17

Resistivity Data of Glass No.15

50Pbo-10Zno-22B₂O₃-10Sio₂-5B₁O₃-3Se (Mole %)

Thickness of the specimen = 0.02 cm

Area of the electrode = 0.36 cm²

Temperature, °K	Resistance, ohms	Resistivity, ohm cm
185	0.78×10^{-1}	1.78×10^{-2}
215	1.20×10^{-1}	2.16×10^{-2}
236	1.34×10^{-1}	2.41×10^{-2}
265	1.487×10^{-1}	2.68×10^{-2}
285	1.552×10^{-1}	2.79×10^{-2}
307	1.928×10^{-1}	3.48×10^{-2}
343	2.2×10^{-1}	3.92×10^{-2}
389	2.79×10^{-1}	5.02×10^{-2}
417	3.19×10^{-1}	5.72×10^{-2}
445	3.87×10^{-1}	6.97×10^{-2}
469	3.75×10^{-1}	6.75×10^{-2}
495	3.01×10^{-1}	5.44×10^{-2}
474	4.528×10^{-1}	8.15×10^{-2}
442	5.25×10^{-1}	9.45×10^{-2}
404	5.00×10^{-1}	9.00×10^{-2}
384	5.348×10^{-1}	9.63×10^{-2}
359	5.87×10^{-1}	9.06×10^{-3}
326	5.36×10^{-1}	9.65×10^{-2}

TABLE 18

Resistivity Data of Glass No 16

 $45\text{PbO}-10\text{ZnO}-22\text{B}_2\text{O}_3-15\text{SiO}_2-5\text{BaO}-3\text{Se}$ (Mole %)

Thickness of the specimen = 0.062 cm.

Area of electrode = 3.40 cm^2

Temperature $^{\circ}\text{K}$	Resistance, ohms	Resistivity ohm.cm.
290	9×10^{11}	4.935×10^{13}
304	7.2×10^{11}	3.948×10^{13}
308	8.33×10^{10}	4.568×10^{12}
338	1×10^{11}	5.484×10^{12}
397	7.895×10^8	4.33×10^{10}
415	1.515×10^8	8.308×10^9
421	1.4×10^8	7.677×10^9
468	1.67×10^7	9.158×10^8
447	4.17×10^7	2.287×10^9
419	2.4×10^9	1.316×10^{11}
373	1.61×10^9	8.829×10^{10}
349	6.92×10^9	3.795×10^{11}
321	4.83×10^{10}	2.649×10^{12}

TABLE 19

Resistivity Data of Glass No 17

50PbO-10ZnO-22B₂O₃-10SiO₂-5Sb₂O₃-3Se (mole %)

Thickness of the specimen = 0.04 cm

Area of electrode = 0.36 cm²

Temperature °K	Resistance Ohms	Resistivity Ohm-cm
328	3.175×10^9	2.857×10^{10}
349	2.294×10^8	2.064×10^9
388	3.00×10^7	2.700×10^8
424	6.33×10^6	5.7×10^7
451	5.00×10^6	4.5×10^7
466	3.03×10^6	2.727×10^7
475	1.96×10^6	1.76×10^7
508	1.191×10^6	1.07×10^7
483	2.5×10^6	2.25×10^7
451	7.67×10^6	6.903×10^7
429	2.23×10^7	2.007×10^8
407	6.67×10^7	6.003×10^8
382	3.06×10^8	2.754×10^9
342	4.546×10^{10}	4.091×10^{11}

TABLE

Resistivity Data of Glass No 18

45PbO-10ZnO-22B₂O₃-15SiO₂-5Sb₂O₃-3Sc (Mole %)

Thickness of the specimen - 0.06

Area of Electrode = 0.76

Temperature °K	Resistance Ohms	Resistivity Ohm-cm
323	3.704×10^1	4.69×10^2
351	4.0×10^1	5.07×10^2
365	3.59×10^1	4.54×10^2
382	3.478×10^1	4.41×10^2
405	4.00×10^1	5.07×10^2
429	3.00×10^1	3.67×10^2
460	2.703×10^1	3.42×10^2
415	5.882×10^1	7.45×10^2
420	5.366×10^1	6.80×10^2
395	5.0×10^1	6.33×10^2
370	6.000×10^2	7.60×10^3
348	5.582×10^2	7.07×10^3
330	4.571×10^2	5.79×10^3
303	4.533×10^2	5.74×10^3
281	1.0×10^3	1.27×10^4
269	1.0×10^3	1.27×10^4
253	8.0×10^2	1.01×10^4
218	7.212×10^2	9.13×10^3
210	8.75×10^2	1.11×10^4

TABLE 21

Switching Data of Sample No. 14

54PbO-10ZnO-22B₂O₃-6SiO₂-3As₂O₃-5Se (101 /)

Thickness = 0.05 Cm

Area = 0.24 Cm²

Temperature °C	Th shold Voltage	'On' State Resistance
78°C	3 v	3 K
92 C	1.6V	20 K
109	1.1V	30 K
152	1.3V	10 K
202	1.7V	15 K
172	4	20 K
148	6.6	22 K
122	11.6	29 K
97	Did not switch up to 16 V	

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